

FORM PTO-1390 (Modified)  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

200741US6PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/719153

INTERNATIONAL APPLICATION NO.  
PCT/FR99/01375

INTERNATIONAL FILING DATE  
JUNE 10, 1999

PRIORITY DATE CLAIMED  
JUNE 10, 1998

TITLE OF INVENTION

SUBSTRATE WITH A PHOTOCATALYTIC COATING

APPLICANT(S) FOR DO/EO/US

Christian MARZOLIN, et al.


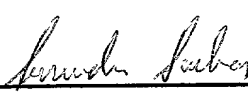
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report  
Notice of Priority  
Drawings ( 2 Sheets )

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) 09/719153		INTERNATIONAL APPLICATION NO. PCT/FR99/01375		ATTORNEY'S DOCKET NUMBER 200741US6PCT	
20. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :					
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO ..... \$860.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$690.00					
<input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$710.00					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$1000.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	18 - 20 =	0	x \$18.00		
Independent claims	1 - 3 =	0	x \$80.00		
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$990.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).			<input type="checkbox"/>	\$0.00	
SUBTOTAL =				\$990.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).			<input type="checkbox"/>	\$0.00	
TOTAL NATIONAL FEE =				\$990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL FEES ENCLOSED =				\$990.00	
				Amount to be refunded	\$
				charged	\$
<input checked="" type="checkbox"/> A check in the amount of \$990.00 to cover the above fees is enclosed.					
<input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
<div> 22850 Surinder Sachar Registration No. 34,423</div>			<div> SIGNATURE C. Irvin McClelland NAME 21,124 REGISTRATION NUMBER Dec. 11 2000 DATE</div>		

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**STOP PCT Rec'd 16 MAR 2001**

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

:

CHRISTIAN MARZOLIN ET AL.

:

SERIAL NO: 09/719,513  
(Based on PCT/FR99/01375)

: ATTN: APPLICATION BRANCH

FILED: DECEMBER 11, 2000

:

FOR: SUBSTRATE WITH A PHOTO-  
CATALYTIC COATING

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to a first examination on the merits, please amend the above-identified  
application as follows:

IN THE SPECIFICATION

Page 1, before line 1, insert: --TITLE OF THE INVENTION--;

between prenumbered lines 1 and 3, insert:

--BACKGROUND OF THE INVENTION

Field of the Invention:--;

between lines 18 and 19, insert: --Discussion of the Background:--;

between lines 35 and 36, insert:

--SUMMARY OF THE INVENTION--.

Page 13, between lines 23 and 24, insert:

--BRIEF DESCRIPTION OF THE DRAWINGS--;

between lines 30 and 31, insert:

--DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

IN THE CLAIMS

Please amend the claims as follows:

Claim 3, lines 1-2, change "either of the preceding claims" to --Claim 1--.

Claim 4, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 5, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 6, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 7, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 8, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 9, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 10, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 11, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 12, lines 1-2, change "one of the preceding claims" to --Claim 1--.

Claim 13, line 2, change "one of the preceding claims" to --Claim 1--.

Claim 14, line 2, change "one of Claims 1 to 12" to --Claim 1--.

Claim 15, line 2, change "one of Claims 1 to 12" to --Claim 1--.

Claim 16, line 2, change "one of Claims 1 to 12" to --Claim 1--.

Claim 17, line 1, line 2, change "one of Claims 13 to 16" to --Claim 13--.

Claim 18, lines 1-2, change "one of Claims 1 to 12" to --Claim 1--.

### IN THE ABSTRACT

Please delete the original Abstract sheet page 21 in its entirety and insert therefor:

#### --ABSTRACT OF THE DISCLOSURE

A substrate, its process of manufacture, and its applications. The substrate includes a fibrous material which is provided, over at least a portion of its surface and/or within its thickness, with a coating with photocatalytic properties including a semi-conducting material with photocatalytic properties of the oxide or sulphide type.--

### REMARKS

Favorable consideration of this application, as presently amended, is respectfully requested.

The present preliminary amendment is submitted to place the above-identified application in more proper format under United States practice. By the present preliminary amendment the specification has been amended to include suggested headings. The claims have been amended to no longer recite any improper multiple dependencies. A new Abstract believed to be in more proper format under United States practice is also submitted herein.

The present application is believed to be in condition for a full and thorough examination on the merits. An early and favorable consideration of the present application is hereby respectfully requested.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



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SUBSTRATE WITH A PHOTOCATALYTIC COATING

The present invention relates to substrates provided with a photocatalytic coating, to the process for producing such a coating and to its various applications.

It relates more particularly to coatings comprising semi-conducting materials based on metal oxide, in particular on titanium oxide, which are capable of initiating radical reactions under the effect of radiation of appropriate wavelength, resulting in the oxidation of organic products. These coatings thus make it possible to confer novel functionalities on the materials which they cover, in particular dirt-repellent, fungicidal, bactericidal, algicidal or odour-controlling properties, optionally in combination with hydrophilic or anti-condensation properties, and the like.

Highly diverse substrates have to date been envisaged, in particular construction materials used in the field of construction or vehicles (windows, facing, cladding or roofing materials, and the like) or materials used in purification processes.

International Patent Applications WO97/10186 and WO97/10185 have thus made known coatings comprising anatase crystallized  $\text{TiO}_2$  with photocatalytic properties, coatings obtained from the thermal decomposition of appropriate organometallic precursors and/or from "precrySTALLIZED"  $\text{TiO}_2$  particles, suited in particular to deposition as a thin layer on glass in order to preserve its optical quality.

Patent Application EP-A-0,306,301 has also made known the use of photocatalytic  $\text{TiO}_2$  on fibrous materials used to purify the air, the deposition of the  $\text{TiO}_2$  being carried out by a process of sol-gel type.

The aim of the invention is then the improvement of these photocatalytic coatings, being targeted in particular at improving their behaviour on any type of substrate and in particular providing them with better adhesion and better durability, very

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particularly on substrates exhibiting characteristics of surface roughness or porosity.

The subject-matter of the invention is first of all a substrate comprising a fibrous material which is provided, over at least a portion of its surface and/or within its thickness, with a coating with photocatalytic properties comprising a semi-conducting material with photocatalytic properties of the oxide or sulphide type in combination with a promoter of adhesion to the said fibrous material.

The semi-conducting material "active" with respect to photocatalysis can be, according to the invention, based on at least partially crystallized metal oxide, for example zinc oxide, tin oxide or tungsten oxide. The preferred example according to the invention relates to titanium oxide at least partially crystallized in anatase form, which is the crystalline phase which confers on  $\text{TiO}_2$  its photocatalytic properties. It can also relate to semi-conductors belonging to the family of the sulphides, also at least partially crystallized, such as zinc sulphide or boron sulphide. (In the continuation of the text, for greater simplicity, mention will be made of titanium oxide, it being understood that the information given will be just as valid for the other semi-conducting materials mentioned above).

The term "fibrous material" is understood to mean, within the meaning of the invention, any material comprising fibres, in particular mineral fibres, more particularly organized fibres made of glass or rock mineral wool, of the type of those used in thermal/sound insulation or to constitute soilless culture substrates. This term "fibrous material" also includes fibres/filaments organized as strands, of the type of the strands used in reinforcement, in particular made of glass.

These base fibrous materials are subsequently incorporated in a "substrate", within the meaning of the invention, in various forms: it can relate to



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felts, mats, webs, "moulds" intended for the insulation of pipes, made of mineral wool, textile strands assembled as fabrics, or non-woven web, made of substrates of paper type, and the like.

5 A photocatalytic coating makes it possible to confer highly advantageous novel functionalities on these known substrates. Thus, the felts/mats of mineral wool mainly used in insulation can be treated only superficially, only on one of their faces, for example, 10 or on each of their faces, and can acquire a dirt-repellent/odour-controlling function on at least one of their treated faces (the visible face and/or the hidden face) in false ceiling structures of buildings, in antinoise screens alongside roads or railways, and the 15 like, the condition laid down being that the photocatalytic coating is accessible to a natural or artificial light source. Still in the field of insulation, the abovementioned "moulds" can also be treated on the inside and/or outside or over their 20 entire thickness, for example, in order to confer on them a dirt-repellent and/or bactericidal or fungicidal function. In the form of mats or of moulds, the substrates treated according to the invention can advantageously be positioned around outlet conduits in 25 any ventilation or air-conditioning system but also by being positioned inside these conduits, these devices being veritable breeding grounds for bacteria, the condition being that it is necessary to provide means for the photocatalytic coating to be exposed to 30 sufficient ultraviolet radiation to be effective: on a visible external face, natural illumination may be sufficient. If not, the substrates have to be combined with artificial illuminating means of the halogen lamp or fluorescent tube type.

35 Another application relates to any system for reflecting and/or scattering natural light or light originating from artificial illuminating means, such as lampshades or curtains, when the substrate is, for example, in the web form.

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The other main application, apart from thermal or sound insulation, of the substrates treated according to the invention relates to the filtration or the purification of fluids.

5 It can relate to any filter used in the filtration of gases, in particular of air, of paper web or filter paper type, used, for example, in the ventilation/air-conditioning systems for dwellings mentioned above or for industrial premises, vehicles or  
10 laboratory rooms with a controlled level of dust, of the "clean" room type.

The term of "filter" covers two notions within the meaning of the invention, both the notion of true filtration, where particles are separated mechanically  
15 from the gas carrying them, and the notion of diffuser, in particular of odour-controlling diffuser, where the gas to be treated is not necessarily forced to pass through the photocatalytic substrate, where it can in particular simply be brought into contact with the  
20 latter, without retaining the suspended particles.

Mention may be made of many other applications of the gas "filters" according to the invention: they can also be used to purify any type of industrial gaseous effluent or any atmosphere of a given public  
25 place or building (as odour-controlling diffuser in the underground, for example). They can in particular make it possible to reduce the "VOC" (volatile organic compounds) level of a given gas stream or of a given atmosphere.

30 The filters, surface-treated or treated throughout their thickness, can become much more effective and much more durable; this is because the treatment according to the invention gives them the ability not only to remove microorganisms but also to  
35 decompose organic residues of fatty type which generally constitute a good part of the particles which gradually block the filter. With the invention, these filters therefore have a longer lifetime. In addition, they have a odour-controlling function.

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It can also relate to filters for liquids.

The liquid filters according to the invention have numerous applications: they can be used for the recycling of wastewater or for the recycling of water from systems for the irrigation of soilless culture substrates (for disinfecting the water). They can also fulfil a function of depollution, in particular depollution of soils, or a function of reprocessing/depolluting industrial liquid effluents.

The advantage of treating according to the invention all these fibrous substrates has been seen. However, to furnish them with a photocatalytic coating was not, initially, very easy. This was because the question arose of the method of deposition of the coating on a substrate which is generally non-smooth, non-flat and of rough and porous type, as well as the question of the durability of this coating.

The solution of the invention consisted in adjusting the way in which it was applied to the substrate, namely superficially or throughout its thickness, according to the applications targeted as a function of requirements, and in rendering the anatase  $\text{TiO}_2$  of the coating, which is responsible for the photocatalytic performance, integral with the fibrous material via an appropriate adhesion promoter. The latter can thus act as "matrix" for the components of the coating which are "active" with respect to the photocatalysis phenomenon.

According to a first alternative form, the titanium oxide is already at least partially precrystallized in anatase form when it is incorporated in the coating, before being deposited on the substrate. It can be introduced into the coating in the form of crystalline particles in colloidal suspension or in the form of a dry powder composed of particles which are optionally more or less agglomerated with one another. This alternative form exhibits the advantage of not imposing a high specific heat treatment on the coating/substrate on which it is deposited ( $\text{TiO}_2$

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crystallizes in the anatase form generally in the vicinity of 400°C).

According to a second alternative form (which can be combined with the first), the titanium oxide originates from the thermal decomposition of precursors, in particular of the organometallic or metal halide type, within the coating. The anatase crystallized  $\text{TiO}_2$  can thus be manufactured "in situ" in the coating, once applied to the substrate, by providing for an ad hoc heat treatment, which must, however, be compatible with the chosen substrate and the chosen adhesion promoter.

As regards the adhesion promoter, the latter can be single or multicomponent, it being possible for its component or components to be organic, inorganic or organic/inorganic "hybrids".

It can thus comprise a silicon-comprising component, in molecular form or in polymeric form, of the silane, silicone or siloxane type, for example. This is because these components exhibit a good affinity with the majority of mineral fibres, glass, rock or even ceramic, affecting the invention. It is even possible, in some cases, to speak of a kind of grafting of the crystallized  $\text{TiO}_2$  to the inorganic fibres by this type of component.

The adhesion promoter can also comprise one or more polymers of organic type. In fact, two scenarios exist: standard organic polymers, for example of the acrylic or phenol-formaldehyde type, or the like, can be chosen. In this case, there is a risk of this component being gradually decomposed by photocatalysis by the  $\text{TiO}_2$ , at least in the (surface) regions of the substrate liable to be exposed to ultraviolet radiation. However, the process can in fact prove to be advantageous in some applications, by thus gradually "releasing" active  $\text{TiO}_2$ . However, it may be preferable to avoid or slow down as far as possible this decomposition by choosing appropriate polymers, generally fluorinated polymers, which are highly

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resistant to photocatalytic attacks, for example of the fluorinated acrylic polymer type, of the polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF) or tetrafluoroethylene-ethylene copolymer (ETFE) type, and the like.

One alternative consists in retaining an adhesion promoter based on organic polymer(s) and in thwarting their decomposition by appropriate additives, in particular belonging to the family of the antioxidants (such as the product sold under the name Irganox by the company Ciba) and/or of the ultraviolet absorbers (such as the product sold under the name Tinuvin by the same company) and/or of stabilizers in the form of sterically hindered amines known under the term "hindered amine light stabilizers" or "HALS".

The adhesive promoter can also comprise at least one metal oxide of the  $\text{TiO}_2$  or  $\text{SiO}_2$  type originating from the thermal decomposition of precursors of the silicon-comprising, organometallic or metal halide type within the coating. In this case, the  $\text{TiO}_2$  or  $\text{SiO}_2$  component is generated in situ in the coating, in particular once applied to the substrate, by an appropriate heat treatment compatible with the substrate. In the case of  $\text{TiO}_2$ , it is not, however, necessary to envisage very high temperatures necessary for an anatase crystallization, if only an adhesion promoter function is being sought: it can perfectly well be amorphous or partially crystallized in various crystalline forms, just like  $\text{SiO}_2$ . It is thus possible to have a coating of the amorphous metal oxide matrix type which fixes the "active" particles of crystallized photocatalytic oxide.

The adhesion promoter can also comprise at least one inorganic component chosen from aluminium phosphates and potassium or calcium aluminosilicates.

One embodiment of the invention consists in that at least one of the two essential components of the coating, namely, on the one hand, the "active" (with regard to photocatalysis) components and, on the

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other hand, the adhesion promoter, forms part of the binder making possible the intrinsic cohesion of the fibrous material.

This is because, if the material is glass or  
5 rock mineral wool of the insulation type, such as that produced by Isover Saint-Gobain, the latter is in numerous applications provided with a binder generally denoted under the name of size and generally applied in the liquid phase by spraying under the fiberizing  
10 devices. The solvent/dispersant is generally aqueous and it evaporates on contact with or in the vicinity of the hot fibres. The agents for sticking the fibres to one another, generally of the resin type, for example phenolic resin, such as urea-phenol-formaldehyde  
15 polymers, cure under hot conditions. One possibility then consists in adding the adhesion promoter and the "active" components to the aqueous medium of the size or even in using/adapting the components of the size in order for them to act simultaneously as binder of the  
20 fibres to one another and of promoter of fibres/"active" components adhesion.

For further details on typical sizing compositions and their method of application to fibres, reference may advantageously be made in particular to  
25 Patents EP-143,050, EP-246,952, EP-305,249, EP-369,848, EP-403,347, EP-480,778 and EP-512,908. However, it should be noted that, in specific applications, the mineral wool can be devoid of binder, for example that composed of relatively fine fibres used to prepare  
30 filter papers, as disclosed, for example, in Patents EP-0,267,092 and EP-0,430,770, or needled felts.

If the material is instead a fibrous material of reinforcing strands or textile strands type, in particular such as that manufactured by Vetrotex, the  
35 cohesiveness of the strands resulting from the assembling of individual filaments under a bushing is generally provided by application of a binder generally denoted under the term of sizing composition. Here again, it is applied in the liquid phase and comprises

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one or more agents "sticking together" the fibres/filaments. It is therefore possible to choose to add the "active" components and/or the adhesion promoter according to the invention to the liquid  
5 medium or to adapt its composition in order to make it act both as interfilament binder and as promoter of strands/"active" components adhesion.

For further details on sizing compositions, reference may advantageously be made in particular to  
10 Patents EP-243,275, EP-394,090, EP-635,462, EP-657,396, EP-657,395, EP-678,485, EP-761,619 and WO-93/18737.

Mention may also be made of Patent WO-98/51633, relating to the deposition of size in two steps under the fiberizing device, size in addition being capable  
15 of polymerizing at room temperature. In this case, it is possible to choose to introduce the material with photocatalytic properties either into the first sizing composition or into the second or into both.

All these sizes mentioned above are generally  
20 applied, using sizing rolls just under the bushing, to the fibrous material still in the form of individual filaments in the course of being gathered together into strands. There also exist binders, intended to ensure the cohesion of mats obtained from a blanket of glass  
25 strands, which are ejected onto continuous or non-continuous strands which have already been sized. Mention may be made, by way of example, of Patent WO-97/21861. The photocatalytic material can be incorporated in this binder, which also acts as  
30 adhesion promoter.

The sizes or binders mentioned above are either in the aqueous phase or in the non-aqueous phase. In the latter scenario, a heat treatment is generally no longer necessary to remove the water, the components  
35 chosen then being chosen so as to be able to polymerize at room temperature. In this case, the incorporation of materials with photocatalytic properties pre-existing independently of any heat treatment is favoured, such as small crystallized titanium oxide particles.

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As mentioned above, the fibrous material according to the invention can therefore be organized in the web (facing, for example), felt or paper form or in various geometric forms (flat or pleated paper type sheets, for example, panel, hollow cylindrical "mould", woven or non-woven web, and the like). The fibrous material can also be in bulk, in the form of optionally graded short fibre or flocks.

The photocatalytic coating of the invention is advantageously applied to the fibrous material so that at least a portion of the "fibres" of the said material (including the notions of fibres, of filaments and of strands) is sheathed with the coating over a thickness of at least 5 nm, in particular over a thickness of the order of 30 to 50 nm.

This sheathing ensures maximum effectiveness of the coating, its photocatalytic activity increasing as it is distributed over a greater specific surface. The preferred thickness takes into account the most commonly encountered mean size of the anatase  $\text{TiO}_2$  crystallites.

Another subject-matter of the invention is the processes for the manufacture of the substrates defined above.

According to a first alternative form, the photocatalytic coating is deposited, in the liquid phase, on the production line itself for the fibrous material. The advantage to this alternative form lies in the fact that the still semi-finished fibrous material can be treated and the best use can be made of the temperature which it is at, for example, resulting in a saving in terms of time and of production cost. Thus, a first embodiment consists in "hot" depositing the coating between the fiberizing devices and the devices for receiving the fibres. The fiberizing devices can consist of glass centrifuging dishes, known as "internal centrifuging devices", such as are disclosed, for example, in Patents EP-0,189,534 and EP-0,519,797, making it possible to fiberize mineral



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wool of glass type, or devices for fiberizing by so-called external centrifuging using a succession of centrifuging wheels, such as are disclosed, for example, in Patents EP-0,465,310 or EP-0,439,385, making it possible to obtain mineral wool of basalt rock type. It can also relate to devices for fiberizing by mechanical drawing, in order to obtain reinforcing glass strands, by air blowing or by steam blowing, according to processes well known to persons skilled in the art. Use is thus made of the fact that the fibres are still at a relatively high temperature by applying the coating, generally in solution/dispersion, in a solvent, for example an aqueous solvent, which evaporates on contact with or in the vicinity of the fibres. The heat can also make it possible to cure the component or components of the adhesion promoter, if they are of the resin type, or to decompose them thermally, if they are of the silicon-comprising precursor or metallic precursor type mentioned above.

As mentioned above, the coating in the liquid phase can be applied at the same time as an optional "binder" of the sizing composition type or even form part of it. It may also be preferable to apply it to the fibrous material before or after the said "binder".

According to a second embodiment of this first alternative form, the photocatalytic coating, still generally in the liquid phase, can be deposited "after" the receiving devices which collect the fibres/filaments or strands resulting from the fiberizing devices and in particular before or during the post-fiberizing heat treatment of the fibrous material. Thus, for mineral wool of insulation type, the receiving devices are generally composed of a suction conveyor belt which gathers together the mineral wool and passes it into a forming oven. It can be judicious to apply the coating between the two devices (fiberizing/receiving), for example superficially, and to use the heat of the oven to cure or complete the coating, if necessary.

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Likewise, in the field of reinforcing glass, the strands are drawn and wound off in the form of spools or cut up under the bushing, after having been appropriately sized, and then generally dried in heated chambers, before being converted and/or used.

As mentioned above, it is therefore possible to deposit the photocatalytic coating just under the bushing, in particular concomitantly with the deposition of the size, in which it can be incorporated. It is also possible to deposit it during the stage of finishing the spooled strands into finished products: it can, for example, relate to the conversion operation targeted at manufacturing mats of chopped strands, in a subsequent operation; it is also possible to deposit it on the downstream line, in particular during the conversion of the continuous strands, gathered together as a blanket, into a mat of continuous strands.

In the last two cases, the photocatalytic coating can be deposited by an ejection system of the adjusted sprayer type, before, during or at the same time as the binder used (or be used in combination with it in the same liquid phase).

According to a second alternative form, the photocatalytic coating is deposited in the liquid phase on the finished fibrous material, in a subsequent operation. What this involves is instead a "cold" treatment, requiring a post-deposition heat treatment in order to evaporate the solvent and optionally to cure or to complete, to constitute the coating.

Whatever the alternative form chosen, the coating can be deposited by different techniques. If the coating comprises "active" anatase crystallized  $\text{TiO}_2$  powder or particles from the start, it is not necessary for the fibrous substrate to be very hot; temperatures of less than  $300^\circ\text{C}$  and even of less than  $200^\circ\text{C}$  may suffice, indeed even room temperature, and therefore temperatures which are found on production lines for the commonest mineral fibrous materials, temperatures

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which are in addition compatible with the sizes for these materials, which are generally organic, at least partly. If, on the other hand, it is necessary to generate anatase  $\text{TiO}_2$  "in situ", it is necessary to envisage temperatures of the order of  $400^\circ\text{C}$ , instead with fibrous materials devoid of binder in the general sense of the term and in a subsequent operation, for example by a process of sol-gel type.

In concrete terms, it is possible to choose to impregnate the fibrous material to the core and to use a technique of "dip-coating" type, where the fibrous material is at least partially immersed in a bath comprising the coating in the liquid phase. It is also possible to choose coating or spraying adapted to a surface treatment. The deposition can also be carried out in a fluid which is non-liquid in the usual sense of the term, for example in a hypercritical fluid.

Another subject-matter of the invention is the application of these treated substrates to thermal/sound insulation or facing materials, with a dirt-repellent, fungicidal, antibacterial or odour-controlling function, or to liquid or gas filters of paper type or of felt or mould type.

Other advantageous details and characteristics of the invention emerge from the description below of non-limiting implementational examples using the following figure:

□ Figure 1: a negative obtained by scanning electron microscopy (SEM) of the surface of a fibrous material treated according to the invention.

All the following examples relate to the deposition of a coating for which the photocatalytic "active" components are made of anatase crystallized  $\text{TiO}_2$ . (It goes without saying that, as mentioned above, the invention applies in the same way to semi-conducting "active" components with photocatalytic properties similar to anatase  $\text{TiO}_2$  and which can be provided in the same form, in particular zinc oxide, tin oxide and tungsten oxide).

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**EXAMPLE 1**

A needled felt (dimensions  $210 \times 297 \times 5 \text{ mm}^3$ ), composed of glass fibres of insulating type obtained by binder-free internal centrifuging and with a relative density of  $55 \text{ kg/m}^3$ , was sprayed with an aqueous  $\text{TiO}_2$  solution, sold under the trade name "TOSol" by Saga Céramics, over its entire thickness.

This solution comprises a dispersion of particles of  $\text{TiO}_2$  crystallized in anatase form, probably composed of crystallite agglomerates, these agglomerates having a mean size of the order of 20 to 80 nm. These particles are therefore the "active" components in terms of photocatalysis. The solution also comprises an organometallic  $\text{TiO}_2$  precursor which will decompose into predominantly amorphous  $\text{TiO}_2$  by heat treatment and which will act as adhesion promoter.

The coating obtained was baked at  $200^\circ\text{C}$  for 2 hours and comprises anatase nanocrystals in an amorphous  $\text{TiO}_2$  matrix. The yellow colour of the filter thus manufactured testifies to the presence of organic compounds originating from the precursor solution. After exposure to ultraviolet A radiation under a dose of  $4 \text{ W/m}^2$  for 2 hours, the yellow colour has completely disappeared, which shows complete decomposition of the residual organic pollutants.

**EXAMPLE 2**

Glass fibre of insulation type obtained by binder-free internal centrifuging was converted by the papermaking route in pure water. The paper obtained, circular with a diameter of 100 mm and a weight per unit area of  $150 \text{ g/m}^2$ , was subsequently impregnated over its entire thickness by dip-coating it in an alcoholic dispersion comprising, by volume, 5% water, 1% tetraethoxysilane (the adhesion promoter) and 1% anatase crystallized  $\text{TiO}_2$  particles with a mean diameter of 30 nm (the "active" components). The paper was dried in the open air and then baked in an oven at  $450^\circ\text{C}$  for 30 minutes. This filter was subsequently placed over an inlet orifice of a fume cupboard. A control filter,

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without anatase  $\text{TiO}_2$ , was placed over the neighbouring orifice. An ultraviolet A lamp shines on these filters at a dose of  $4 \text{ W/m}^2$ . After the cupboard had been operated for 15 days, the treated filter was still white, whereas the untreated filter was fouled.

### EXAMPLE 3

A composition for the sizing of glass wool of insulation type obtained by internal centrifuging was manufactured by mixing:

- 10  $\Rightarrow$  55 g of resin obtained by condensation of phenol and formaldehyde in an initial formaldehyde/phenol molar ratio of approximately 3.2/1, which condensation is carried out conventionally with a catalyst in the form of sodium hydroxide at 5.5% by weight with respect
- 15 to the phenol,
  - $\Rightarrow$  45 g of urea,
  - $\Rightarrow$  3 g of aminopropyltrimethoxysilane,
  - $\Rightarrow$  0.3 g of ammonium sulphate,
  - $\Rightarrow$  6 g of 30% by volume aqueous ammonia,
- 20  $\Rightarrow$  1200 g of a 25% by weight dispersion in water of anatase crystallized  $\text{TiO}_2$  particles,
- $\Rightarrow$  34 litres of water.

The  $\text{TiO}_2$  particles have a mean diameter of approximately 45 nm. The adhesion promoter for the latter can be regarded as all the other components of the size and very particularly the silane.

This composition was sprayed via the sizing ring during a fiberizing of the glass wool under the centrifuging dishes. The felt obtained was subsequently passed on the line into an oven at  $180^\circ\text{C}$  for 2 minutes. The felt has a weight per unit area of  $560 \text{ g/m}^2$  and a loss on ignition of 1.4% (measurement known to a person skilled in the art, expressed by weight, by heating the felt at a temperature sufficient to remove all the organic compounds). A  $1 \times 20 \times 40 \text{ mm}^3$  piece was removed and placed in a vessel with 20 g of an aqueous solution comprising 1 g/l of ethanol and 15 mg/l of hydrogen peroxide. The solution was shone on by a mercury lamp producing  $4 \text{ W/m}^2$  of ultraviolet radiation and the

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concentration of hydrogen peroxide was monitored by colorimetry. Oxidation of ethanol by hydrogen peroxide, catalysed by the anatase  $\text{TiO}_2$  irradiated with ultraviolet radiation, is observed.

5           The photocatalytic activity of the felt was evaluated by measuring the weight of hydrogen peroxide  $\text{H}_2\text{O}_2$  in milligrams which disappears per gram of fibre in the solution and per hour. The result was 4.4 mg  $\text{H}_2\text{O}_2/\text{g.fibre/hour}$ .

10           Samples of  $200 \times 300 \times 200 \text{ mm}^3$ , coming from the same treatment, have been subjected to naturel sun exposure. Gradually the yellow colour, that is characteristic for the resin used, disappeared from the exposed surfaces and to some centimetres in depth. This  
15           vanishing clearly indicated a degradation of the phenolic resin used as well as the penetration of the photocatalytic effect inside the material. Similar results were obtained und controlled UVA radiation of  $4\text{W/m}^2$  for 24 hours.

20           **EXAMPLE 4**

          280 g of glycidoxypropyltrimethoxysilane were added to a sizing composition similar to that of Example 3 (other silane combining with the above to act as adhesion promoter). The felt obtained by fiberizing  
25           and sizing with this solution was stoved at  $180^\circ\text{C}$  for 2 minutes. The felt has a weight per unit area of  $1 \text{ kg/m}^2$  and a loss on ignition of 1.4%. The measurement of the photocatalytic activity, carried out as in Example 3, gave a value of 3 mg  $\text{H}_2\text{O}_2/\text{g.fibre/hour}$ .

30           Figures 1, 2 and 3 show, in three different scales, a fibre covered with the photocatalytic coating. Figure 1 shows more particularly a fibre, at the surface of which is clearly distinguished a sheathing of  $\text{TiO}_2$  particles, two successive  
35           magnifications being shown in Figures 2 and 3.

          In conclusion, it is found that the coating of the invention exhibits a proven photocatalytic activity on fibres, whatever the implementational alternative forms:

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Example 1 illustrates a deposition "in a subsequent operation", outside the line for the production of mineral wool, using "precrySTALLIZED"  $\text{TiO}_2$  particles and an inorganic adhesion promoter manufactured in situ, on a fibrous substrate of felt type.

Example 2 also illustrates a deposition "in a subsequent operation", on a fibrous substrate of paper type, with precrySTALLIZED  $\text{TiO}_2$  particles and a silicon-comprising adhesion promoter.

Finally, Examples 3 and 4 illustrate an in-line hot deposition under the fiberizing devices, which will make possible treatment within the thickness of the fibrous material, with "precrySTALLIZED"  $\text{TiO}_2$  particles and adhesion promoters of the family of the silanes in combination with the components of a standard size, in the aqueous phase.

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Photocatalytic webs based on mineral fibres were manufactured using a plant which makes it possible to carry out the impregnation of a glass web in a sizing solution, the application of suction to this web (in order to remove the excess binder) and, finally, its baking in an oven, the entire process being carried out in-line and continuously. The web is unwound on a conveyor belt, conveyed into the sizing bath via an impregnation roller, passes above a negative-pressure tank (suction device) and is finally conveyed by a second conveyor belt into the baking oven.

Various types of photocatalytic media were synthesized according to this process, in accordance with the following examples:

15 EXAMPLE 5: A medium for the purification of gases

An  $40 \text{ g/m}^2$  glass web was impregnated with an aqueous solution comprising 3.1% of Glymo (glycidoxypopyltrimethoxysilane) and 2.9% of titanium dioxide nanoparticles at a rate of 0.2 m/min.

20 This web, having been subjected to a suction equivalent to a water column of 35 mm, was subsequently baked at  $200^\circ\text{C}$  for 10 minutes. The resulting loss on ignition is 7%.

Measurements of effectiveness in the gas phase were then carried out under the following conditions:  $150 \times 200 \text{ mm}^2$  of the resulting product were placed in a cylindrical photocatalysis reactor. This reactor is composed of an axial UV-A lamp (365 nm), around which is surrounded, with a spacing of 1 cm, the photocatalytic medium in 3 layers, and of an aluminium jacket. The intensity of the irradiation on the web is  $1 \text{ mW/cm}^2$ . The reactor is inserted in a closed circuit, with recirculation, the gas passing through the medium from the inside of the closed cylinder over the web towards the outside.

The volume of the cell (photocatalysis reactor) is 0.9 l and that of the complete circuit (immobilized volume) is one litre. The experiments consisted in

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evaluating the photocatalytic decomposition of n-hexane.

To do this, various amounts of n-hexane (ranging up to 2000 ppm in air) were injected into the circuit, the flow rate of the latter being regulated at 1 l/min. At regular intervals, 50 µl samples of gas were withdrawn in order to measure the concentration of n-hexane present in the circuit.

It was shown that the direct decomposition by UV of n-hexane is negligible, just as its absorption by the medium. In contrast, n-hexane is virtually 100% decomposed in less than one hour when it passes through the photocatalytic medium, though under weak UV irradiation.

**EXAMPLE 6: A medium for liquid purification**

According to the same process, a 60 g/m<sup>2</sup> glass web was impregnated in an aqueous solution comprising 1 g/l of A-100 silane and 5 g/l of titanium dioxide (sold under the name P25 by Degussa) held in suspension by appropriate means.

The web was impregnated in-line at 0.6 m/min, the excess binder having been removed under a negative pressure of 90 mm of water column. The product was baked at 300°C for 30 minutes. Measurements of effectiveness in the liquid phase were then carried out in order to describe this material.

A circular specimen of web (diameter 100 mm) was placed at mid-height in a 300 ml beaker. The bottom and the edges of the receptacle having been rendered opaque, the beaker is illuminated by a bank of UV-A lamps (365 nm) delivering a power of 3.5 mW/cm<sup>2</sup> to the web. An aqueous solution (deionized water) comprising 10 mg/l of phenol is poured into the device and is kept stirred magnetically. The decrease in concentration of the phenol is then monitored, samples being withdrawn at regular time intervals, by a UV spectrometer sold by Dr Lange.

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It could be confirmed that virtually 100% of the phenol had disappeared over approximately at most one hour.

5 More generally, these last two examples show the advantage of the use of a web formed of photocatalytic mineral fibres, such as those manufactured, in purification operations in a liquid medium as in the gas phase.

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CLAIMS

1. Substrate comprising a fibrous material which is provided, over at least a portion of its surface and/or within its thickness, with a coating with photocatalytic properties comprising a semi-conducting material with photocatalytic properties of the oxide or sulphide type, in particular titanium oxide at least partially crystallized in anatase form, the said material being used in combination with a promoter of adhesion to the said fibrous material.
2. Substrate according to Claim 1, characterized in that the semi-conducting material of the titanium oxide type is introduced into the coating in the form of particles in colloidal suspension or in the form of a powder.
3. Substrate according to either of the preceding claims, characterized in that the titanium oxide originates from the thermal decomposition of organometallic or metal halide precursor(s) within the coating.
4. Substrate according to one of the preceding claims, characterized in that the adhesion promoter is organic, inorganic or organic/inorganic hybrid, single- or multicomponent.
5. Substrate according to one of the preceding claims, characterized in that the adhesion promoter comprises a silicon-comprising component of the silane, silicone or siloxane type.
6. Substrate according to one of the preceding claims, characterized in that the adhesion promoter comprises one or more organic polymers, in particular acrylic polymers or fluorinated polymers, optionally in combination with additives belonging to the family of the antioxidants and/or of the ultraviolet absorbers and/or of the stabilizers of the "HALS" type.
7. Substrate according to one of the preceding claims, characterized in that the adhesion promoter comprises at least one metal oxide of the  $\text{TiO}_2$  or  $\text{SiO}_2$

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type originating from the thermal decomposition of silicon-comprising, organometallic or metal halide precursor(s) within the coating.

8. Substrate according to one of the preceding claims, characterized in that the adhesion promoter comprises at least one inorganic component chosen from aluminium phosphates and potassium or calcium aluminosilicates.

9. Substrate according to one of the preceding claims, characterized in that the adhesion promoter forms part of the binder making possible the cohesion of the fibrous material, in particular of the sizing type for mineral wool or sizing type for reinforcing strands or binder type for a mat obtained from reinforcing strands.

10. Substrate according to one of the preceding claims, characterized in that the mineral fibrous material comprises mineral wool of the insulation type and/or glass strands of the reinforcing type.

11. Substrate according to one of the preceding claims, characterized in that the fibrous material is organized in the web, felt, mould, paper or bulk material form.

12. Substrate according to one of the preceding claims, characterized in that the coating with photocatalytic properties sheaths at least a portion of the fibres of the fibrous material over a thickness of at least 5 nm, in particular of between 30 and 50 nm.

13. Process for the manufacture of the substrate according to one of the preceding claims, characterized in that the coating with photocatalytic properties is deposited in the liquid phase on the production line for the fibrous material, in particular between the fiberizing devices, of the centrifuging dish, device for fiberizing by external centrifuging, device for fiberizing by mechanical drawing, device for fiberizing by air blowing or device for fiberizing by steam blowing type, and the devices for receiving the fibres, optionally before, with or after the deposition of the

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binder in the liquid phase of the fibres to one another, of the sizing composition type.

14. Process for the manufacture of the substrate according to one of Claims 1 to 12, **characterized in** that the coating with photocatalytic properties is deposited in the liquid phase on the production line for the fibrous material downstream of the devices for receiving the fibres resulting from the fiberizing devices, in particular before the optional heat treatment/conditioning devices of the stove type.

15. Process for the manufacture of the substrate according to one of Claims 1 to 12, **characterized in** that the coating with photocatalytic properties is deposited in the liquid phase on the production line or outside the production line for the fibrous material during the operation of conversion of the latter into the finished product, in particular during the operation of conversion of blankets of reinforcing strands into mats.

16. Process for the manufacture of the substrate according to one of Claims 1 to 12, **characterized in** that the coating with photocatalytic properties is deposited in the liquid phase on the finished fibrous material and then the said material is subjected to a heat treatment.

17. Process according to one of Claims 13 to 16, **characterized in that** the coating is deposited in the fluid phase, in particular the liquid phase, by spraying, coating or dip coating.

18. Application of the substrate according to one of Claims 1 to 12 to thermal/sound insulation materials or to liquid or gas filters, purifiers or diffusers, in order to confer on them dirt-repellent, fungicidal, bactericidal, algicidal or odour-controlling properties.

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PATENT

**SUBSTRATE WITH A PHOTOCATALYTIC COATING**

**Applicant: SAINT-GOBAIN RECHERCHE**

**ABSTRACT**

The subject-matter of the invention is a substrate comprising a fibrous material which is provided, over at least a portion of its surface and/or within its thickness, with a coating with photocatalytic properties comprising a semi-conducting material with photocatalytic properties of the oxide or sulphide type.

Another subject-matter of the invention is its process of manufacture and its applications.

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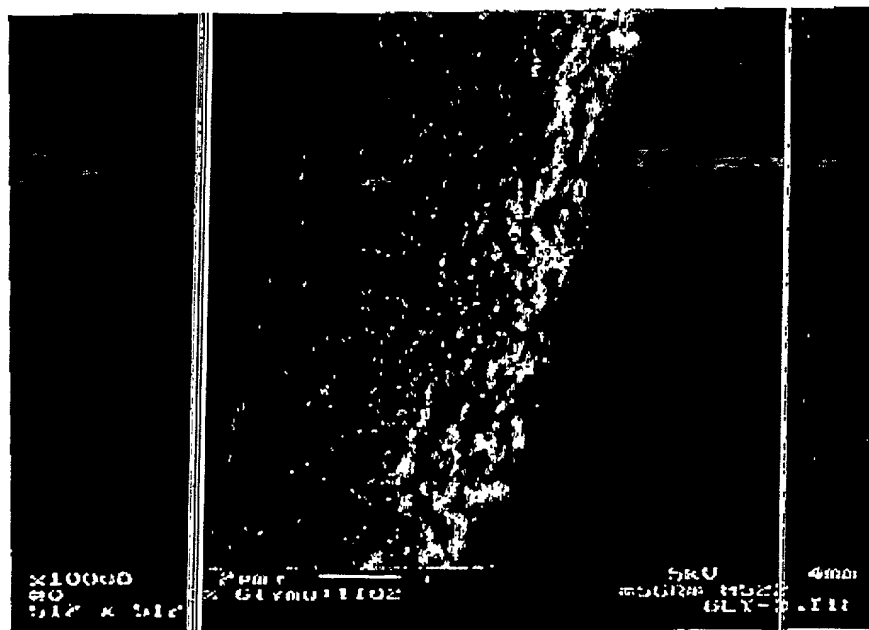


FIGURE 1

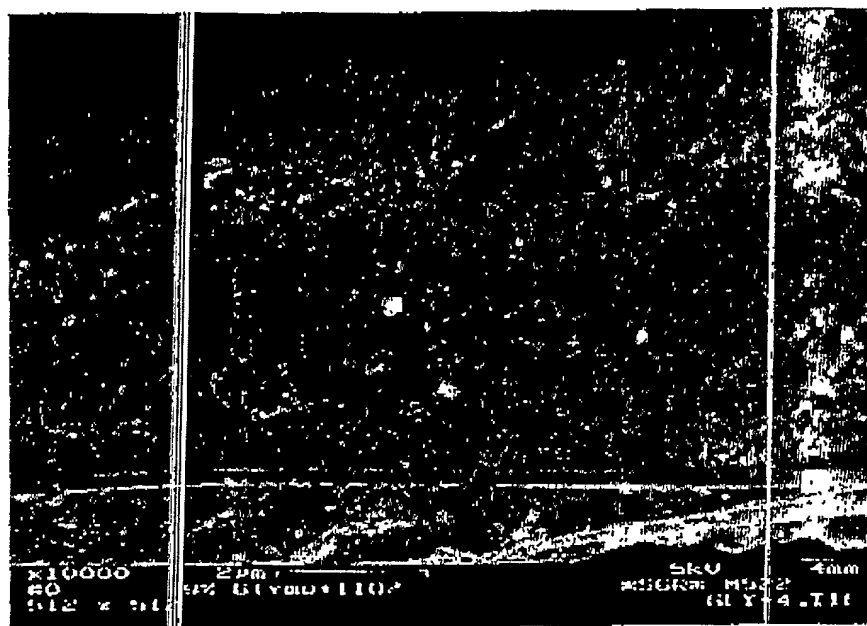


FIGURE 2

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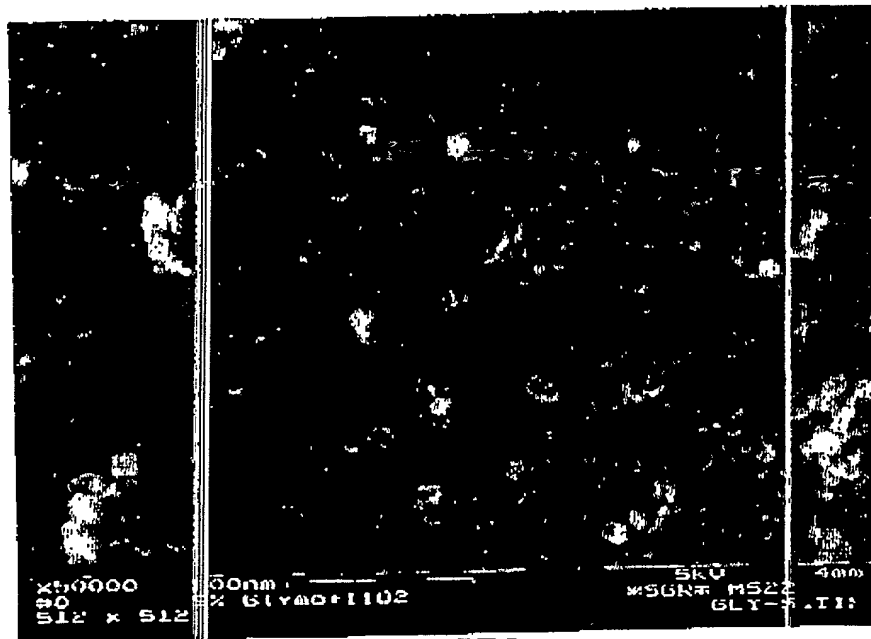


FIGURE 3

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# Declaration and Power of Attorney for Patent Application

## Déclaration et Pouvoirs pour Demande de Brevet

### French Language Declaration

En tant l'inventeur nommé ci-après, je déclare par le présent acte que

As a below named inventor, I hereby declare that:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom

My residence, post office address and citizenship are as stated next to my name

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SUBSTRATE WITH A PHOTOCATALYTIC COATING

et dont la description est fournie ci-joint à moins

the specification of which:

☐ ci-joint

☐ is attached hereto.

☐ a été déposée le \_\_\_\_\_

☒ was filed on December 11, 2000

sous le numéro de demande des Etats-Unis ou le numéro de demande international PCT

as United States Application Number or PCT International Application Number

\_\_\_\_\_ et modifiée le

09/719,153 and was amended on

\_\_\_\_\_ (le cas échéant).

\_\_\_\_\_ (if applicable).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

## French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Demande(s) de brevet antérieure(s) dans un autre pays.

Priority claimed  
Droit de priorité  
revendiqué

98/07276                      FRANCE  
(Number)                      (Country)  
(Numéro)                      (Pays)

10 June 1998  
(Day/Month/Year Filed)  
(Jour/Mois/Année de dépôt)

☒                      ☐  
Yes                      No  
Oui                      Non

\_\_\_\_\_  
(Number)                      (Country)  
(Numéro)                      (Pays)

\_\_\_\_\_  
(Day/Month/Year Filed)  
(Jour/Mois/Année de dépôt)

☐                      ☐  
Yes                      No  
Oui                      Non

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below

\_\_\_\_\_  
(Application No.)                      (Filing Date)  
(N° de demande)                      (Date de dépôt)

\_\_\_\_\_  
(Application No.)                      (Filing Date)  
(N° de demande)                      (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application

PCT/FR99/01375                      10 June 1999  
(Application No.)                      (Filing Date)  
(N° de demande)                      (Date de dépôt)

\_\_\_\_\_  
(Status) (patented, pending, abandoned)  
(Statut) (breveté, en cours d'examen, abandonné)

\_\_\_\_\_  
(Application No.)                      (Filing Date)  
(N° de demande)                      (Date de dépôt)

\_\_\_\_\_  
(Status) (patented, pending, abandoned)  
(Statut) (breveté, en cours d'examen, abandonné)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## French Language Declaration

POUVOIRS. En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec l'Office des brevets et des marques. (mentionner le nom et le numéro d'enregistrement).

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

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Nom complete de l'unique ou premier inventeur	Full name of sole or first inventor
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	<i>[Signature]</i>
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Nationalité	Citizenship
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	same as above
Nom complete du second co-inventeur, le cas echeant	Full name of second joint inventor, if any
	<b>Arnaud MARCHAT</b>
Signature de l'inventeur	Second inventor's signature
	<i>[Signature]</i>
Date	Date
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(Fournier les mêmes renseignements et la signature de tout co-inventeur supplémentaire)

(Supply similar information and signature for third and subsequent joint inventors.)

## French Language Declaration

<b>Nom complet du troisième co-inventeur, le cas échéant</b>	<b>Full name of third joint inventor, if any</b> Xavier TALPAERT
<b>Signature de l'inventeur</b>	<b>Third Inventor's signature</b> 
<b>Date</b>	<b>Date</b> 01/17/2001
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<b>Adresse Postale</b>	<b>Post Office Address</b> same as above

<b>Nom complet du quatrième co-inventeur, le cas échéant</b>	<b>Full name of fourth joint inventor, if any</b>
<b>Signature de l'inventeur</b>	<b>Fourth Inventor's signature</b>
<b>Date</b>	<b>Date</b>
<b>Domicile</b>	<b>Residence</b>
<b>Nationalité</b>	<b>Citizenship</b>
<b>Adresse Postale</b>	<b>Post Office Address</b>

<b>Nom complet du cinquième co-inventeur, le cas échéant</b>	<b>Full name of fifth joint inventor, if any</b>
<b>Signature de l'inventeur</b>	<b>Fifth Inventor's signature</b>
<b>Date</b>	<b>Date</b>
<b>Domicile</b>	<b>Residence</b>
<b>Nationalité</b>	<b>Citizenship</b>
<b>Adresse Postale</b>	<b>Post Office Address</b>

<b>Nom complet du sixième co-inventeur, le cas échéant</b>	<b>Full name of sixth joint inventor, if any</b>
<b>Signature de l'inventeur</b>	<b>Sixth Inventor's signature</b>
<b>Date</b>	<b>Date</b>
<b>Domicile</b>	<b>Residence</b>
<b>Nationalité</b>	<b>Citizenship</b>
<b>Adresse Postale</b>	<b>Post Office Address</b>

(Fournir les mêmes renseignements et la signature de tout co-inventeur supplémentaire.)

(Supply similar information and signature for third and subsequent joint inventors.)